

POLYMER ELECTROLYTE SYSTEM

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation-in-part of U.S. Patent Application serial number (not yet assigned), filed concurrently herewith; entitled "Polymer Electrolyte for Electrochemical Cell" and incorporated herein in its entirety.

[0002] This application is related to U.S. Patent Application serial number 10/367,013 filed on February 13, 2003 and entitled "Cross-Linked Polysiloxanes," which claims priority to U.S. Provisional Patent Application serial number 60/374374, filed on April 22, 2002 and entitled "Cross-Linked Polysiloxanes"; and is related to U.S. Patent Application Serial Number 10/104,352 titled "Solid Polymer Electrolyte." Each of the above applications is assigned to the assignee of the current application and is hereby incorporated by reference herein in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0003] This invention was made with United States Government support under NIST ATP Award No. 70NANB043022 awarded by the National Institute of Standards and Technology (NIST). The United States Government has certain rights in this invention pursuant to NIST ATP Award No. 70NANB043022 and pursuant to Contract No. W-31-109-ENG-38 between the United States Government and the University of Chicago representing Argonne National Laboratory, and NIST 144 LM01, Subcontract No. AGT DTD 09/09/02.

FIELD

[0004] The present invention relates to electrolytes for electrochemical devices, and more particularly to electrolytes including siloxane polymers.

BACKGROUND

[0005] The increased demand for lithium secondary batteries has resulted in research and development to improve the safety and performance of these batteries. These batteries often employ carbonate based liquid electrolytes associated with high degrees of volatility, flammability, and chemically reactivity. A variety of siloxane polymer based electrolytes have been developed to address these issues. However, many of these electrolytes have a low ionic conductivity that limits their use in lithium primary and secondary batteries and capacitors to applications that do not require high rate performance. As a result, there is a need for electrolytes that include siloxane-based polymers and have an increased ionic conductivity.

SUMMARY

[0006] The invention relates to an electrochemical device including a blended electrolyte. The blended electrolyte includes one or more polyalkylene glycol dialkyl ethers, one or more alkali metal salts, and one or more siloxane polymers.

[0007] The invention also relates to a method of forming an electrochemical device. The method includes forming a blended electrolyte that includes one or more polyalkylene glycol dialkyl ethers, one or more alkali metal salts, and one or more siloxane polymers. The method also includes activating at least one anode and at least one cathode with the blended electrolyte.

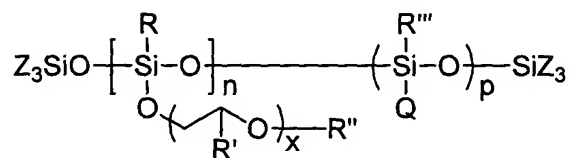
[0008] The one or more polyalkylene glycol dialkyl ethers can include one or more polyethylene glycol dialkyl ethers. The one or more siloxane polymers can include one or more poly(siloxane-g-ethylene oxide)s. At least one of the one or more siloxane polymers can be cross-linked.

[0009] The electrolyte can include an interpenetrating network. In some instances, a network polymer and one or more other polymers interact so as to form the interpenetrating network. The one or more other polymers are selected from the group consisting of the one or more polyalkylene glycol dialkyl ethers and the one or more siloxane polymers. In some instances, the electrolyte includes an interpenetrating network and one or more of the siloxane polymers is cross-linked.

[0010] In some instances, the electrolyte includes one or more matrix polymers. The one or more matrix polymers can include at least one component selected from the group consisting of polyacrylonitrile, poly(vinylidene fluoride), poly(vinylidene fluoride-co-hexafluoropropylene), polystyrene, polyvinyl chloride, poly(alkyl methacrylate), poly(alkyl acrylate), styrene butadiene rubber (SBR), and poly(vinyl acetate).

[0011] The one or more siloxane polymers can include at least one material selected from the group consisting of those represented by the following Formulas I - VI:

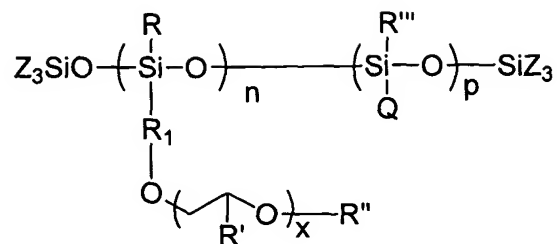
[0012] Formula I



[0013]

[0014] where R and R'' are alkyl groups and R' is hydrogen or an alkyl group; R''' is alkyl or hydrogen; Q is hydrogen or a cross-linker; p is 0 or greater than 0; n is from 1 to 100; x is from 1 to 30; and Z is an alkyl or aryl group.

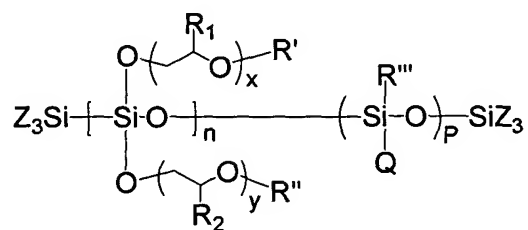
[0015] Formula II:



[0016]

[0017] where, R and R''' are alkyl groups and R' is hydrogen or an alkyl group; R₁ is a spacer made up of one or more CH₂ groups; R''' is alkyl or hydrogen; Q is hydrogen or a cross-linker; p is 0 or greater than 0; n is from 1 to 100; x is 2 to 25; and Z is an alkyl or aryl group;

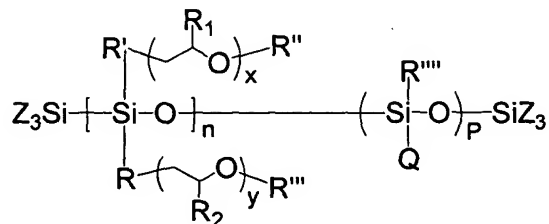
[0018] Formula III:



[0019]

[0020] wherein R'' and R' are alkyl groups; R₁ and R₂ are hydrogen or alkyl group; R''' is alkyl or hydrogen; Q is hydrogen or a cross-linker; p is 0 or greater than 0; n is from 1 to 100; x is from 1 to 30; y is from 1 to 30; Z is alkyl or aryl group;

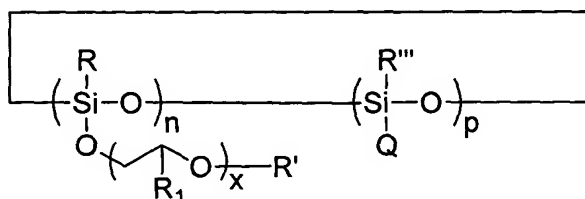
[0021] Formula IV:



[0022]

[0023] wherein R and R' are spacers made up of one or more CH₂ groups; R'' and R''' are alkyl group; R₁ and R₂ are hydrogen or alkyl group; R'''' is alkyl or hydrogen; Q is hydrogen or a cross-linker; p is 0 or greater than 0; n is from 1 to 100; x is from 1 to 30; y is from 1 to 30; Z is alkyl or aryl group; and

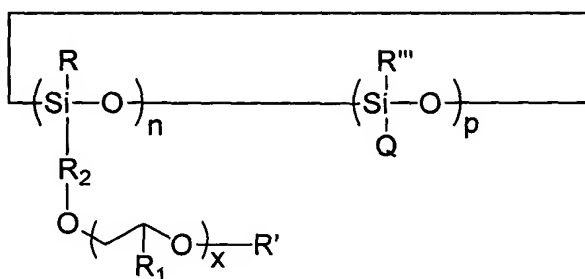
5 [0024] Formula V:



[0025]

[0026] wherein R and R' are alkyl groups; R₁ is hydrogen or alkyl group; R''' is alkyl or hydrogen; Q is hydrogen or a cross-linker; p is 0 or greater than 0; n is from 1 to 100; x is from 1 to 30; R' is an alkyl or aryl group; and

10 [0027] Formula VI:



[0028]

[0029] wherein R and R' are alkyl groups; R₁ is hydrogen or an alkyl group; R₂ is a spacer made up of one or more CH₂ groups; R''' is alkyl or hydrogen; Q is hydrogen or a cross-linker; p is 0 or greater than 0; n is from 1 to 100; x is from 1 to 30; R' is an alkyl or aryl group.

15

[0030] The electrolyte can include two or more polysiloxanes. In some instances, the electrolyte includes two or more siloxane polymers chosen from those

represented by Formulas I - VI. For example, a first siloxane represented by Formula I or II may be used as the main siloxane in the blend to keep the viscosity low, and a second siloxane represented by Formula III or IV may be used for its preferential interaction with PEGDME to enhance voltage stability of the blend. As another example, a highly conductive siloxane may be combined with a low viscosity siloxane to improve wetting of the electrodes, leading to increased capacity and enhanced cycling properties.

BRIEF DESCRIPTION OF THE FIGURES

[0031] Figure 1 is an ionic conductivity versus temperature curve for an electrolyte system of 80 wt% poly(siloxane-g-3 ethylene oxide) and 20 wt% of PEG₅DME.

[0032] Figure 2 is a current versus voltage curve showing electrochemical stability of an electrolyte system of 80 wt% of poly(siloxane-g-3 ethylene oxide) and 20 wt% PEG₅DME, compared with that of a PEG₅DME electrolyte.

[0033] Figure 3 is a voltage versus capacity curve for lithium cells.

[0034] Figure 4A through Figure 4F are NMR spectra for a blended electrolyte and for the components of the blend.

DETAILED DESCRIPTION

[0035] The invention relates to an electrolyte for use in electrochemical devices. The electrolyte includes a blend of one or more siloxane polymers and one or more polyalkylene glycol dialkyl ethers. In some instances, at least one siloxane polymer includes polyalkylene oxide side chains and at least one polyalkylene glycol dialkyl ether is a polyethylene glycol dimethyl ether (PEGDME). The components of the blended electrolyte can interact with one another to provide an electrolyte that

dissolves lithium salts and has an ionic conductivity around 5×10^{-4} S/cm near room temperature. Further, the blended electrolytes can improve the voltage instability often associated with the use of PEGDME. For instance, some embodiments of the blended electrolyte have an electrochemical stability window of over 4.5 V (vs. lithium).

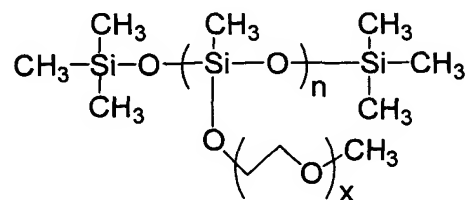
Further, the blended electrolytes can often be easily synthesized. For instance, many siloxane polymers suitable for use in the electrolyte can be synthesized through dehydrogenation reactions or by hydrosilylation.

[0036] The above advantages provide an electrolyte that is suitable for use in battery applications requiring high rate performance. Other suitable applications for the electrolyte include batteries for electric or hybrid vehicles, load leveling installations, submarines, satellites, emergency power backup, and other high capacity applications.

[0037] An example of the blended electrolyte was used to generate the ionic conductivity versus temperature curve shown in Figure 1. The blended electrolyte included 80 wt% of poly(siloxane-g-3 ethylene oxide) and 20 wt% of PEG₅DME where wt% is the percentage of the total polymer weight in the electrolyte. Formula VII represents the structural formula of the poly(siloxane-g-3 ethylene oxide) when $n = 8$ and $x \approx 3$. Formula VIII represented the structural formula of the PEG₅DME when $n = 5$. The blended electrolyte also included a $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ salt mixed with the poly(siloxane-g-3 ethylene oxide) and PEG₅DME so as to provide a $[\text{EO}]/[\text{Li}]$ ratio of 15. In determining the $[\text{EO}]/[\text{Li}]$ ratio, $[\text{EO}]$ is the molar concentration in the electrolyte of the active oxygens in the one or more siloxane polymers and the one or more polyalkylene glycol dialkyl ethers. Because $[\text{EO}]$ is directed to active oxygens, there are x active oxygens in the Formula I, III, V, or VII side chains while there are $x+1$ oxygens in each

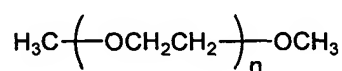
side chain constructed according to Formula II, IV, or VI. $[Li]$ is the molar concentration of the lithium in the electrolyte.

[0038] Formula VII:



[0039]

5 [0040] Formula VIII:



[0041]

[0042] Figure 1 shows the ionic conductivity versus temperature curve for the 80 wt% poly(siloxane-g-3 ethylene oxide) and 20 wt% PEG₅DME blended electrolyte including Li(CF₃SO₂)₂N at a [EO]/[Li] ratio of 15 as described above. Figure 1 also shows an ionic conductivity versus temperature curve for an electrolyte including Li(CF₃SO₂)₂N mixed with only the polysiloxane described above (Formula VII, n = 8 and x ≈ 6) at a [EO]/[Li] ratio of 15. The ionic conductivities were determined from ac impedance curves of 2030 button cells assembled by injecting the electrolyte between two stainless steel discs with a glass filter (750 micron thick) to prevent a short circuit. The measurement frequency range was from 1 MHz to 10 Hz. The blended electrolyte shows a higher ionic conductivity than the polysiloxane through the measured temperature range. Further, the blended electrolyte system shows high ionic conductivity of approximately 5×10⁻⁴S/cm at 37°C.

[0043] Figure 2 illustrates a current versus voltage curve for the 80 wt% poly(siloxane-g-3 ethylene oxide) and 20 wt% PEG₅DME electrolyte with Li(CF₃SO₂)₂N

at a [EO]/[Li] ratio of 15 as described above. Figure 2 also shows a current versus voltage curve for an electrolyte including $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ mixed with only the PEG₅DME described above at a [EO]/[Li] ratio of 15 and for an electrolyte including $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ mixed with only the polysiloxane described above (Formula VII, $n = 8$ and $x \approx 6$) at a [EO]/[Li] ratio of 15. The curves shown in Figure 2 were determined by cyclic voltammetry in 2030 button cells assembled by sandwiching a glass filter containing the polymer electrolyte between a stainless steel disc as a working electrode and lithium metal disc as counter and reference electrode, known as the two electrodes method. The PEG₅DME electrolyte decomposed from about 3.5 V while the blended electrolyte remained stable up to 4.5 V. Although the blended electrolyte has an improved ionic conductivity, the blended electrolyte showed a voltage stability close to the stability performance of the polysiloxane.

[0044] Figure 3 shows the voltage versus capacity curve for the 80 wt% of poly(siloxane-g-3 ethylene oxide) and 20 wt% of PEG₅DME electrolyte with $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ at a [EO]/[Li] ratio of 15 as described above. Figure 3 also shows a voltage versus capacity curve for an electrolyte including $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ mixed with only the polysiloxane described above (Formula VII, $n = 8$ and $x \approx 6$) at a [EO]/[Li] ratio of 15. The data were developed using 2030 button cells assembled with lithium metal as an anode and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ as a cathode. The composition of the cathode is shown in Table 1. The effective cell area was 1.6 cm^2 . The charge rate was C/20 (0.1mA). The cell with the blended electrolyte comprising 80 wt% poly(siloxane-g-3 ethylene oxide) and 20 wt% PEG₅DME did not show any decomposition peak in entire charge/discharge voltages, 3.0~4.1V. Accordingly, Figure 2 and Figure 3 illustrate that the blended electrolyte does not exhibit the voltage instability associated with PEGDME electrolytes.

Component	$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$	PVDF	Graphite	Carbon black
[wt%]	84	8	4	4

Table 1 Cathode Composition

[0045] Figure 1 through Figure 3 illustrate that the blended electrolyte can have a conductivity higher than an electrolyte having only the siloxane polymer and still not have the voltage instability associated with the use of PEGDME. These benefits likely result from a molecular level interaction of the blend components. The ^1H and ^{13}C NMR spectra for a blend and the components of the blend are shown Figure 4A through Figure 4F. Figure 4A and Figure 4B are, respectively, the ^1H and ^{13}C NMR spectra for 100 wt% poly(siloxane ethylene oxide) represented by Formula VII when $n = 8$ and $x \approx 3$. Figure 4C and Figure 4D are, respectively, the ^1H and ^{13}C NMR spectra for a PEGDME represented by Formula VIII with $n = 5$. Figure 4E and Figure 4F are, respectively, the ^1H and ^{13}C NMR spectra for a blended electrolyte including 50 wt% poly(siloxane ethylene oxide) and 50 wt% PEGDME.

[0046] Table 2 summarizes the results of NMR spectra presented in Figure 4A through Figure 4F. Column A shows the NMR peak locations for the poly(siloxane-ethylene oxide). Column B shows the NMR peak locations for the PEGDME. The column labeled C shows the NMR peak locations for blend of 50 wt% poly(siloxane-ethylene oxide) and 50 wt% PEGDME. The values listed in column C are different from those in the corresponding column A and column B, suggesting molecular level interactions between the poly(siloxane-ethylene oxide) and the PEGDME. This interaction may explain the enhanced properties of the blended electrolyte evident in Figure 1 through Figure 3.

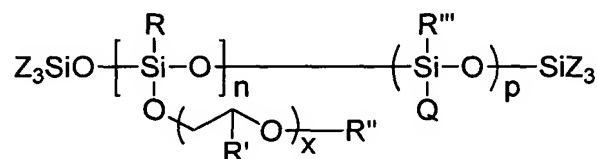
NMR	A (ppm)	B (ppm)	C (ppm)
^1H	-0.14 ~ -0.04 (m)*		-0.06 ~ 0.07
^1H	3.12 (s)	3.16 ~ 3.21 (m)	3.23 (s)
^1H	3.27 ~ 3.45 (m)	3.35 ~ 3.37 (m) 3.44 ~ 3.51 (m)	3.38 ~ 3.54 (m)
^1H	3.62 (br. s)		3.70 (br. s)
^{13}C	-6.15 ~ -4.47 (m)		-4.99 ~ -4.18 (m)
^{13}C	1.20 (s)		1.49 (s)
^{13}C	58.42 (s)	58.62 (s)	58.81 (s)
^{13}C	61.07~61.36 (m)	61.28 (s)	61.31~61.61 (m)
^{13}C	69.93 ~ 70.18 (m)	70.18 ~ 70.27 (m)	70.20 ~ 70.46
^{13}C	71.48 ~ 71.83 (m)	71.63 (s)	71.76 ~ 72.08 (m)
^{13}C	72.19 (s)	72.31 (s)	72.40 (s)

*(m: multiple peaks): (s: single peak): (br. s: broad single peak):
+: downfield shifts; -: upfield shifts

Table 2.

[0047] Suitable siloxane polymers for use with the blended electrolyte
5 include, but are not limited to, siloxane polymers represented as Formulas I to VI.

[0048] Formula I:



[0049]

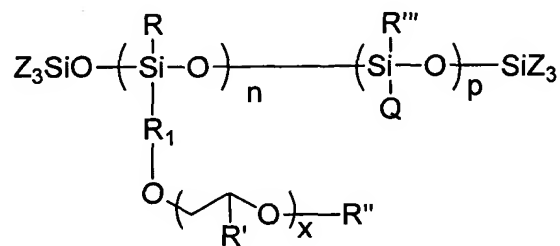
[0050] where, R and R'' are alkyl groups and R' is hydrogen or an alkyl
group; R''' is alkyl or hydrogen; Q is hydrogen or a cross-linker; p is 0 or greater than 0;
10 n is from 1 to 100; x is from 1 to 30; and Z is an alkyl or aryl group. When p is greater
than 0, the n silicons and the p silicons can be positioned adjacent to one another or the p
silicons can be mixed among the n silicons.

[0051] Suitable methods for generating siloxane polymers according to
Formula I with p = 0 include, but are not limited to, dehydrogenation reactions between a
15 polysiloxane precursor having main chain silicons bonded to hydrogen and a side chain

precursor including a poly(alkylene oxide) moiety and a terminal -OH group in the presence of mild catalysts such as aryl borate, potassium carbonate, and metal carbonate based catalysts. Methods for generating siloxane polymers according to Formula I are taught in U.S. Patent Application serial number 10/167,940, filed June 12, 2002; entitled

5 “Nonaqueous Liquid Electrolyte” and incorporated herein by reference in its entirety. Suitable methods for generating siloxane polymers according to Formula I with $p > 0$ and Q as a hydrogen include, but are not limited to, performing the dehydrogenation reaction with an excess of the polysiloxane precursor to ensure that a portion of the main chain

10 [0052] Formula II



[0054] where, R and R'' are alkyl groups and R' is hydrogen or an alkyl group; R₁ is a spacer made up of one or more CH₂ groups; R''' is alkyl or hydrogen; Q is hydrogen or a cross-linker; p is 0 or greater than 0; n is from 1 to 100; x is 2 to 25; and Z

15 is an alkyl or aryl group. When p is greater than 0, the n silicons and the p silicons can be positioned adjacent to one another or the p silicons can be mixed among the n silicons.

[0055] Suitable methods for generating siloxane polymers according to Formula II with $p = 0$ include, but are not limited to, hydrosilylation between a polysiloxane precursor having main chain silicons bonded to hydrogen and an allyl

20 terminated side chain precursor that includes a poly(alkylene oxide) moiety. An example side chain precursor includes an allyl terminated polyethylene glycol methyl

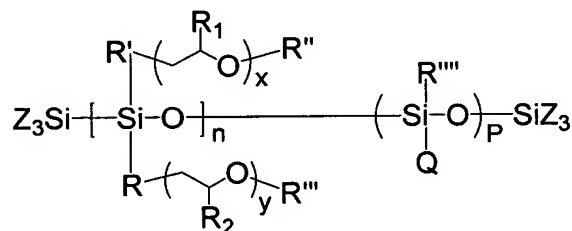
$$\text{Z}_3\text{Si}-\left[\text{Si}-\text{O}\right]_n-\left(\text{Si}-\text{O}\right)_p-\text{SiZ}_3$$

$\begin{array}{c} \text{R}_1 \\ | \\ \text{O}-(\text{CH}_2)_x-\text{O}-\text{R}' \\ | \\ \text{Si} \end{array}$
 $\begin{array}{c} \text{R}''' \\ | \\ (\text{Si}-\text{O})_p-\text{SiZ}_3 \\ | \\ \text{Q} \end{array}$
 $\begin{array}{c} \text{O}-(\text{CH}_2)_y-\text{O}-\text{R}'' \\ | \\ \text{Si} \end{array}$

[0059] Suitable methods for generating siloxane polymers according to Formula III with $p = 0$ include, but are not limited to, dehydrogenation reactions between a polysiloxane precursor having main chain silicons bonded to two hydrogens and side chain precursors including a poly(alkylene oxide) moiety and a terminal -OH group in the presence of mild catalysts such as aryl borate, potassium carbonate, and metal carbonate based catalysts. Suitable methods for generating siloxane polymers according to

Formula III with $p > 0$ and Q as a hydrogen include, but are not limited to, performing the dehydrogenation reaction with an excess of the polysiloxane precursor to ensure that a portion of the main chain silicons remain bonded to hydrogen.

[0060] Formula IV:



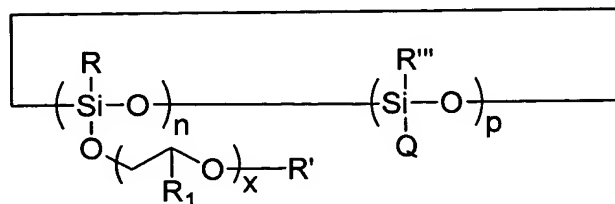
[0061]

[0062] wherein R is a spacer made up of one or more CH₂ groups; R' is a spacer made up of one or more CH₂ groups; R'' and R''' are alkyl group; R₁ and R₂ are hydrogen or alkyl group; R'''' is alkyl or hydrogen; Q is hydrogen or a cross-linker; p is 0 or greater than 0; n is from 1 to 100; x is from 1 to 30; y is from 1 to 30; and Z is alkyl or aryl group. When p is greater than 0, the n silicons and the p silicons can be positioned adjacent to one another or the p silicons can be mixed among the n silicons.

[0063] Suitable methods for generating siloxane polymers according to Formula IV with $p = 0$ include, but are not limited to, hydrosilylation between a polysiloxane precursor having main chain silicons bonded to two hydrogens and an allyl terminated side chain precursor that includes a poly(alkylene oxide) moiety. Suitable methods for generating siloxane polymers according to Formula IV with $p > 0$ and Q as a hydrogen include, but are not limited to, performing the hydrosilylation reaction with an excess of the polysiloxane precursor to ensure that a portion of the main chain silicons remain bonded to hydrogen. Methods for generating siloxane polymers according to Formula IV with $p > 0$ and C as a hydrogen are taught in U.S. Provisional Patent Application serial number 60/374,374, filed April 22, 2002 and entitled "Cross-Linked

Polysiloxanes” and in U.S. Provisional Patent Application serial number 10/367,013, filed February 13, 2003 and entitled “Cross-Linked Polysiloxanes”, each of which is incorporated herein in its entirety.

[0064] Formula V:



[0065]

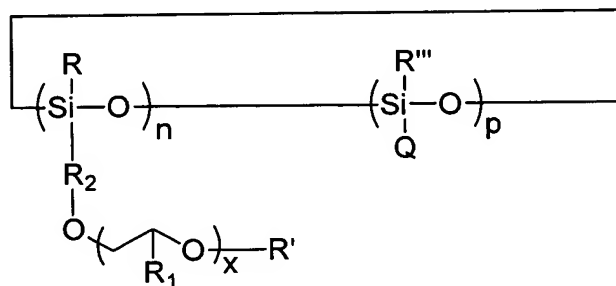
[0066] wherein R and R' are alkyl groups; R₁ is hydrogen or alkyl group; R''' is alkyl or hydrogen; Q is hydrogen or a cross-linker; p is 0 or greater than 0; n is from 1 to 100; x is from 1 to 30; and R' is an alkyl or aryl group, preferably a methyl, ethyl, propyl, or phenyl group. When p is greater than 0, the n silicons and the p silicons can be positioned adjacent to one another or the p silicons can be mixed among the n silicons.

[0067] Suitable methods for generating siloxane polymers according to Formula V with p = 0 include, but are not limited to, dehydrogenation reactions between a cyclic polysiloxane precursor having main chain silicons bonded to hydrogen and side chain precursors including a poly(alkylene oxide) moiety and a terminal -OH group in the presence of mild catalysts such as aryl borate, potassium carbonate, and metal carbonate based catalysts. Methods for generating siloxane polymers according to Formula V with p = 0 are taught in U.S. Provisional Patent Application serial number 60/446,848, filed February 11, 2003 and entitled “Polymer Electrolyte for Electrochemical Cell” and in PCT application number PCT/US03/08779, filed March 20, 2003 and entitled “Polymer Electrolyte for Electrochemical Cell”, each of which is incorporated herein in its entirety. Suitable methods for generating siloxane polymers according to Formula V with p > 0

and Q as a hydrogen include, but are not limited to, performing the dehydrogenation reaction with an excess of the polysiloxane precursor to ensure that a portion of the main chain silicons remain bonded to hydrogen.

[0068]

Formula VI



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[0069]

[0070] wherein R and R' are alkyl groups; R₁ is hydrogen or an alkyl group; R₂ is a spacer made up of one or more CH₂ groups; R''' is alkyl or hydrogen; Q is hydrogen or a cross-linker; p is 0 or greater than 0; n is from 1 to 100; x is from 1 to 30; R' is an alkyl or aryl group preferably a methyl, ethyl, propyl, or phenyl group. When p is greater than 0, the n silicons and the p silicons can be positioned adjacent to one another or the p silicons can be mixed among the n silicons.

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[0071]

Suitable methods for generating siloxane polymers according to Formula VI with p = 0 include, but are not limited to, hydrosilylation between a cyclic polysiloxane precursor having main chain silicons bonded to hydrogen and an allyl terminated side chain precursor that includes a poly(alkylene oxide) moiety. Suitable methods for generating siloxane polymers according to Formula VI with p > 0 and Q as a hydrogen include, but are not limited to, performing the hydrosilylation reaction with an excess of the polysiloxane precursor to ensure that a portion of the main chain silicons remain bonded to hydrogen. Methods for generating siloxane polymers according to Formula IV are taught in U.S. Patent Application serial number (not yet assigned), filed

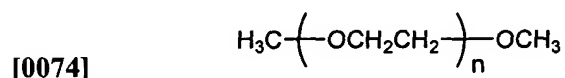
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concurrently herewith, entitled "Polymer Electrolyte for Electrochemical Cell" and incorporated herein in its entirety.

[0072] A suitable polyalkylene glycol dialkyl ether for use with the blended electrolyte includes, but is not limited to polyethylene glycol dimethyl ethers (PEGDME) represented by Formula IX.

[0073] Formula IX:



[0075] wherein $n = 3$ to 8.

[0076] Suitable polyalkylene glycol dialkyl ethers for use with the blended electrolyte can have a molecular weight of less than 1,000 g/mol. The content of polyalkylene glycol dialkyl ether in a liquid polymer electrolyte is about 0.5 to 99.5 wt%, but preferably about 20 wt% to about 60 wt%.

[0077] Suitable salts for use with the blended electrolyte include, but are not limited to, alkali metal salts including lithium salts. Examples of specific lithium salts include LiClO_4 , LiBF_4 , LiAsF_6 , LiPF_6 , LiCF_3SO_3 , $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, $\text{Li}(\text{CF}_3\text{SO}_2)_3\text{C}$, $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$, lithium alkyl fluorophosphates, lithium bis(chelato)borates, and a mixture thereof. The blended electrolyte is preferably formed so as to have an $[\text{EO}]/[\text{Li}]$ ratio in a range of 5 to 50. When the $[\text{EO}]/[\text{Li}]$ ratio is larger than 50, the ionic conductivity of the resulting polymeric electrolyte can become undesirably low because few carrier ions are in the solid polymer electrolyte. When the $[\text{EO}]/[\text{Li}]$ ratio is smaller than 5, the lithium salt is not sufficiently dissociated in the resulting polymeric electrolyte and the aggregation of lithium ions can confine the ionic conductivity.

[0078] One or more of the polymers in the blended electrolyte can be cross-linked. For instance, compounds according to Formula I through Formula VI with a portion of the main chain silicons bonded to hydrogen can serve as cross-linking precursors. The hydrogen bonded silicons can serve as cross-linker binding sites.

5 Suitable ratios of p:n for polysiloxanes having side chains according to Formula I through Formula VI include, but are not limited to, ratios in a range of 1:4 to 1:200, in a range of 1:6 to 1:100, or in a range of 1:6 to 1:70. The n + p silicons can be less than or equal to the total number of silicons in the main chain of the polysiloxane. The hydrogen-bonded silicons need not be positioned adjacent to one another along the main chain but

10 can be distributed among the silicons bonded to sidechains.

[0079] A siloxane polymer having one or more main chain silicons bonded to a hydrogen can be reacted with a cross-linking agent to generate a cross-linked polysiloxane. Suitable cross-linking agents include, but are not limited to, compounds terminated with two or more allyl groups. Examples of suitable cross-linking agents

15 include diallyl-terminated siloxane, diallyl terminated polysiloxanes, diallyl terminated alkylene glycols and diallyl terminated poly(alkylene glycol)s. Suitable cross-linking agents can be represented by the formula, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{R}_3-\text{CH}_2-\text{CH}=\text{CH}_2$, where R_3 is a moiety selected from the group consisting of $\text{O}-(\text{CH}_2\text{CH}_2\text{O})_q$ and $\text{Si}-\text{O}-(\text{Si}-\text{O})_k-\text{Si}$, where q is at least 4 and less than 30, and k is at least 5 and less than 30. These cross-linkers

20 can be generated as disclosed in U.S. patent application serial number 10/367,013. When these cross-linking agents are employed to cross-link a siloxane polymer having a portion of the main chain silicons bonded to a hydrogen, the Si-H bonds in the main chain of the siloxane polymer are replaced with a bond between the silicon and a terminal carbon on the cross-linking agent. Accordingly, the cross-linker represented by the Q in

25 Formula I - Formula VI can be represented by the formula, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{R}_3-\text{CH}_2-\text{CH}_2-$

CH₂-, where R₃ is a moiety selected from the group consisting of O-(CH₂CH₂O)_q and Si-O-(Si-O)_k-Si, where q is at least 4 and less than 30, and k is at least 5 and less than 30.

[0080] In some instances, a catalyst is required to catalyze the interaction between the siloxane polymer and the cross-linking agent. Suitable catalysts include, but are not limited to, platinum catalysts such as Karlstedt's catalyst and H₂PtCl₆. In some instances, the siloxane polymer interacts with the cross-linking agent in the presence of an inhibitor to slow the interaction enough to permit handling prior to viscosity changing. Suitable inhibitors include, but are not limited to, dibutyl maleate. In some instances, heat is also required during the interaction process of the siloxane polymer with the cross-linking agent.

[0081] In some instances, the blend can be formed by mixing the one or more siloxane polymers and the one or more polyalkylene glycol dialkyl ethers. When the electrolyte is to include one or more cross-linked polymers, the one or more cross-linked polymers can be cross-linked in the presence of one or more other polymers that form the electrolyte blend. In some instances, one or more siloxane polymers are cross-linked in the presence of one or more polyalkylene glycol dialkyl ethers.

[0082] A blend having the cross-linked polymers can be used in a liquid or gel form. In some instances, heating can solidify a blended electrolyte having a cross-linked polymer. The cross-linking mechanism often determines whether or not the blended electrolyte will solidify upon heating. A blended electrolyte that is solidified can be used as a solid electrolyte.

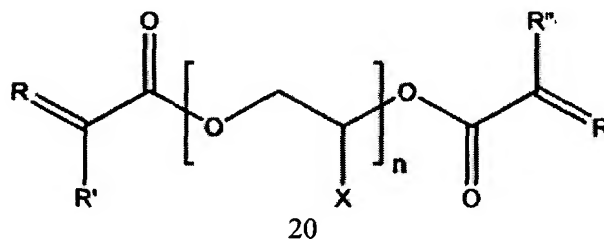
[0083] The blended electrolyte can include an interpenetrating network. For instance, one or more of the polymers in the blended electrolyte can interact with a

network polymer so as to form an interpenetrating network. The interpenetrating network can further enhance the electrochemical stability of the blended electrolyte.

[0084] An electrolyte having an interpenetrating network can be formed by the interpenetrating polymerization method. In some instances, an electrolyte having an interpenetrating network can be formed by polymerizing and/or cross-linking one or more network polymers in the presence of the blended electrolyte. Alternatively, the interpenetrating network can be formed by polymerizing and/or cross-linking one or more network polymers and one or more blended electrolyte polymers in the presence of one another.

[0085] Suitable network monomers for forming the network polymer include, but are not limited to, acrylates and methacrylates. Acrylates and/or methacrylates having one or more functionalities can homopolymerize to form a polyacrylate and/or a polymethacrylate network polymer. Acrylates and/or methacrylates having two or more functionalities can both polymerize and cross-link to form a cross-linked polyacrylate network polymer and/or to form a cross-linked polymethacrylate network polymer. In some instances, acrylates and/or methacrylates having four or more functionalities are a preferred network monomer. Suitable acrylates include, but are not limited to, poly(alkylene glycol) dialkyl acrylate. Suitable methacrylates include, but are not limited to, poly(alkylene glycol) dialkyl methacrylate. Formula X can represent a suitable network monomer for forming the network polymer.

[0086] Formula X:

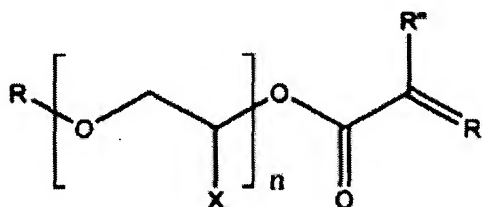


[0087]

[0088] wherein R represents a group selected from an alkyl group having 1 to 10 carbon atoms; each of R' and R'' represents hydrogen or a group selected from an alkyl group having 1 to 10 carbon atoms and/or an alkenyl group having 2 to 12 carbon atoms; X is hydrogen or a methyl group; and n represents a numeral of 1 to 15.

5 [0089] When a monomer that cross-links is employed to form the network polymer, a control monomer can be employed to control cross-linking density. Formula XI represents a suitable control monomer for use with a cross-linking monomer represented by Formula X.

[0090] Formula XI:



10 [0091]

[0092] where each of R and R' represents a group selected from an alkyl group having 1 to 10 carbon atoms; R'' represents hydrogen or a group selected from an alkyl group having 1 to 10 carbon atoms and/or an alkenyl group having 2 to 12 carbon atoms; X is hydrogen or a methyl group; and n represents a whole number from 1 to 20.

15 [0093] A blended electrolyte having an interpenetrating network can be formed by combining the blended electrolyte polymers, monomers for forming one or more network polymer, one or more radical initiators, and one or more alkali metal salts so as to form a precursor solution. Suitable alkali metal salts include, but are not limited to, LiClO₄, LiBF₄, LiAsF₆, LiPF₆, LiCF₃SO₃, Li(CF₃SO₂)₂N, Li(CF₃SO₂)₃C, 20 LiN(SO₂C₂F₅)₂, lithium bis(chelato)borate including lithium(oxalato)borate (LiBOB), and lithium alkyl fluorophosphates. Suitable radical initiators include, but are not

limited to, thermal initiators including azo compounds such as azoisobutyronitrile, peroxide compounds such as benzoylperoxide, and bismaleimide. In some instances, a control monomer is also added to the precursor solution to control the cross-linking density of the network monomer. A film of the precursor solution can be formed on a substrate. Suitable substrates include, but are not limited to, porous media and/or electrode surfaces. Suitable porous media include, but are not limited to, polyolefin separators, nonwoven separators and polycarbonate separators. The substrate can then be heated and solidified.

[0094] In the interpenetrating network formed using the monomers represented by Formula X, the network polymer is formed from a monomer that homopolymerizes and cross-links. A network polymer suitable for the interpenetrating network can be formed using other precursors. For instance, the network polymer can be formed from monomers and cross-linking agents that are different from one another. Further, the monomers can heteropolymerize.

[0095] Other examples of methods of forming an interpenetrating network and electrochemical cells including electrolytes with interpenetrating network are described in U.S. Patent application serial number 10/104,352, filed on March 22, 2002, entitled "Solid Polymer Electrolyte and Method of Preparation" and incorporated herein by reference in its entirety.

[0096] Additionally, the blended electrolyte can be added to a solution including a matrix polymer such as polyacrylonitrile, poly(vinylidene fluoride), poly(vinylidene fluoride-co-hexafluoropropylene), polystyrene, polyvinyl chloride, poly(alkyl methacrylate), poly(alkyl acrylate), styrene butadiene rubber (SBR), poly(vinyl

acetate), and mixtures thereof. In some instances, a solvent in the solution can be evaporated to form a plasticized electrolyte film.

[0097] EXAMPLE 1

[0098] A positive electrode was formed by mixing the components of 84 wt%
 5 LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (Fuji Chem.), 8wt% poly(vinylidene fluoride) (PVDF) (Kureha), 4
 wt% SFG-6 graphite (Timcal), and 4wt% carbon black (Shawinigan) with N-methyl
 pyrrolidone to form a paste. The paste was cast onto Al foil and placed in an oven
 adjusted at 75°C for 5 hrs. The positive electrode was formed by pressing the dried
 material by use of a roll press. The final thickness of the positive electrode was 66 µm.

10 **[0099]** A negative electrode was formed by mixing the components of 92 wt%
 MAG-10 graphite (Sumitomo) and 8 wt% PVdF (Kureha) with N-methyl pyrrolidone to
 form a paste for negative electrode. The paste was cast onto a substrate and placed in an
 oven adjusted at 75°C for 5 hrs. The negative electrode was formed by pressing the
 dried material by use of a roll press. The final thickness of the negative electrode was
 15 52 µm.

[00100] A polysiloxane according to Formula VII with n = 8 and x = 3 was
 synthesized for use in an electrolyte. The polysiloxane was synthesized by employing a
 dehydrogenation reaction between HO-(CH₂-CH₂O)₃-CH₃ and a polysiloxane precursor
 having 8 main chain silicon atoms that are each bonded to a methyl group and a hydrogen.
 20 The dehydrogenation reaction was performed in the presence of a
 tris(pentafluorophenyl)borane [(C₆F₅)₃B] catalyst, using toluene as a reaction solvent. A
 variety of solvents could be alternatively used for this purpose.

[00101] The polysiloxane (Formula VII with n = 8 and x = 3), PEGDME
 (Formula VIII, wherein n=5, Aldrich Chem. Co.), and Li(CF₃SO₂)₂N (3M Co.) were

mixed together to form a blended electrolyte having 80 wt% polysiloxane, 20 wt% of PEG₅DME and a [EO]/[Li] ratio of 15. The mixture was stirred at least 1 hr to be a homogeneous and transparent blend. An electrochemical cell was fabricated by soaking the electrodes the blended electrolyte. A porous PE separator was interposed between the two electrodes to fabricate a 2032 button cell. The cell was stored at 37°C for testing. The effective area of positive electrode was 1.6 cm² and the estimated cell capacity was around 2 mAh.

[00102] EXAMPLE 2

[00103] An electrolyte including an interpenetrating network can be fabricated by mixing poly(siloxane-g-ethylene oxide) (Formula VII, wherein n=8 and x=3) and PEGDME (Formula VIII, wherein n=5, Aldrich Chem. Co.), and poly(ethylene glycol) dimethacrylate (PEGDMA, M_n= ca. 550, Aldrich Chem. Co.), and then dissolving LiTFSI salt (3M Co.) and a benzoyl peroxide thermal initiator (BPO, Aldrich Co.) in the mixture. After vacuuming the mixture to remove bubbles, it can be cast onto a plate and placed in an oven at 70°C for an hour to initiate the network formation by PEGDMA.

[00104] The solid and liquid blended electrolytes described above can be used in electrochemical devices. For instance, the blended electrolytes can be used as the electrolyte of batteries, capacitors, and hybrid capacitor/batteries. As an example, the blended electrolyte can be applied to batteries in the same way as carbonate-based electrolytes. Batteries with a liquid blended electrolyte can be fabricated by injecting the electrolyte into a spiral wound cell or prismatic type cell. The polymer electrolyte can be also coated onto the surface of electrodes and assembled with a porous separator to fabricate a single or multi-stacked cell that can enable the use of flexible packaging.

[00105] An example of a suitable lithium battery construction includes one or more lithium metal oxide cathodes, porous separators, and one or more anodes made of carbon, lithium metal, or combinations thereof. Cathodes may include Li_xVO_y , LiCoO_2 , LiNiO_2 , $\text{LiNi}_{1-x}\text{Co}_y\text{Me}_z\text{O}_2$, $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$, $\text{LiMn}_{0.3}\text{Co}_{0.3}\text{Ni}_{0.3}\text{O}_2$, LiFePO_4 , LiMn_2O_4 , LiFeO_2 , $\text{LiMc}_{0.5}\text{Mn}_{1.5}\text{O}_4$, vanadium oxide, wherein Me is Al, Mg, Ti, B, Ga, Si, Mn, Zn, and Mc is divalent metal such as Ni and Co, Fe, Cr, or Cu. Negative electrodes may include graphite, soft carbon, hard carbon, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, tin alloys, silica alloys, intermetallic compounds, lithium metal, lithium metal alloys, and combinations thereof.

[00106] Other embodiments, combinations and modifications of this invention will occur readily to those of ordinary skill in the art in view of these teachings. Therefore, this invention is to be limited only by the following claims, which include all such embodiments and modifications when viewed in conjunction with the above specification and accompanying drawings.